Volcanic Manifestations
Methods of Sampling and Analysis by Gas Chromatography.
Detection and Quantification Limits.
Analytical Error.

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Abstract
Chemical analyses of volcanic fluids can give information about status of a certain volcano. Relative inexpensive instrumentations may quickly provide useful information. Continuous monitoring of well defined chemical parameters may let the researchers achieve encouraging results in order to produce an attempt to predict future volcanic eruptions. The methods used are mainly two: collection of residual gases and total gases. Both are valid, but for different use. In residual gases one can analyze ratio gas/steam, minus and major components but no carbon monoxide because interference with sodium idroxide. In total gas is difficult to analyze minus components but it’s good for carbon monoxide and isotopic composition in carbon dioxide. In both sampling methods the problem is to choose a good way for sampling. We shows the methods we consider the best in use. Another problems is to minimize analytical error. It depends from the quality of instrumentation and the quality of methods we use. We describe the methods in use in IGG laboratories that give good results, according with quality of instrumentation, quality of standard and reproducibility. We think that may exist other valid methods to collect and analyze samples. The methods we describe are just a starting point, it depends on the ability of researchers and operators to find methods valid for particular sites. In addition are described preparation of bottles for sampling different kinds of natural manifestations. In addition to this some problems can comes from the pressure inside the bottles. We solve the problem with a particular apparatus self made for working at very low pressure, even under one hundred mbar.

Introduction
In performing analytical determinations [1] geochemists often encounter problems right from the stages of sampling. Methodologies for fluid collection are varied and, at times, rather improvised. Familiarity with the methods normally adopted can prove invaluable to anyone deciding to tackle such an undertaking.
The purpose of this technical manual is to describe some methods of sampling and gas chromatographic and chemical analyses of geothermal and volcanic fluids as well as those originating in other low-enthalpy natural manifestations. A particular attention is given to preparation and choose of metals or glasses for the pipe useful for collecting volcanic fluids. The gases considered are the following: CO₂, H₂S, SO₂, Ar, O₂, He, H₂, CH₄, N₂, CO, N₂O, H₂O, NH₃, HCl, HF, C₂H₆, unsaturated C₂, C₃H₈, C₃H₆, iso-C₄H₁₀, n-C₄H₁₀, iso-C₄H₈, n-C₄H₈.

Materials required for fluid sampling
The term “fluid” is used herein to refer to the vapor and/or all gaseous components issuing from a geothermal or fumarole manifestation. Some essential equipment for the collection procedure are: several meters of heat-resistant silicone tubing of various diameters; a 100 cc plastic gas syringe; a glass and Teflon “T” tap; a suitable number of double-valved glass sample holders for collecting the “total” gas and degassed and vacuumized, single-valved-valved glass sample holder with a suitable amount of 4 N NaOH (normally 50 cc); four funnels - two plastic and two metal, 10 and 25 cm in diameter; two pipes - a metal one
(preferably titanium) and a quartz one, perforated at its end; two or three glass traps of about 250 cc; two Dewar flasks, and if possible, some ice dry (alternatives: water and ice, ether or water); alcohol; an indelible marker; various plastic pipe fittings; scissors; screwdriver; pliers; metal clamps; a notebook; pens and pencils.

Preparing the sample holder
When a double-valved glass sample holder (Fig. 1) is used for collecting total gas, a lubricant and sealant grease with the followings characteristics must be used: high adhesion under vacuum with a very low vapor pressure; chemical unreactivity; and good lubricating capacity. Moreover, it must be able to maintain these properties at both high and low temperatures for a period of at least six months.
At the laboratory of the I.G.G. Apiezon N or T grease is used. Although the “T” type is more resistant to heat, it does not maintain its desirable properties as long as type “N.”

Fig. 1 Double-valves glass sample holder fit for total gas sampling

It is generally preferable to lubricate the taps on site immediately before sampling, especially if reaching the site involves air travel (to avoid alteration of the grease’s properties by the extreme cold often found in baggage compartments).
The proper sample holder for collecting residual gases has a valve with Teflon piston (Fig. 2).

Fig. 2 Sample holder for collecting residual gases with a valve with teflon piston
The sodium hydroxide must not contain CO₂ (Labeled: CO₂-free NaOH), and the solution must be prepared immediately before being transferred to the sample holder so as to avoid absorption of atmospheric CO₂. Small amounts of sodium hydroxide in tablet form are added to preheated water up to the desired concentration; a silicone rubber tube is then introduced into the beaker and the desired quantity of solution aspirated directly into the previously vacuumized sample holder. The sample holder must be vacuumized by interposing a trap with liquid nitrogen or dry ice between the vacuum pump and the sample holder to prevent sodium hydroxide from entering the rotor. The resulting vacuum will correspond to the vapor pressure of 4 N NaOH, that is, about 15 mbar. In case of volcanic fluids, in the sodium solution we added 20 cc of ZnOH 1 N for separation of S²⁻ (precipitation as ZnS) from SO₃²⁻ (dissolved in solution).

Sampling
The main problems in collecting volcanic samples fluid are: contamination with air during sampling or subsequent stages and the non-proportional loss of one or more constituents due to chemical interactions (example, the reaction in humid environments between H₂S and O₂) or physical ones (e.g., the solubilization of CO₂, SO₂ and H₂S in the liquid phase during separation of the gas from the vapor in the sampled fluid). There are two types of gas samples, one termed total gas, which is generally dry and contains all components soluble in the condensate water, except for SO₂ and NH₃. The other is called residual gas, where the minor components are found in the gaseous phase together with CO₂, H₂S and SO₂ in the liquid phase, initially made up of 4 N NaOH. This type of sampling can be used to measure the ratio between the gas and the vapor. In case of low ratio of gas/steam there are problems to have the right amount of gas for gaschromatographic analyses. In this case in our opinion is better to have a low pressure with enough volume of gas then viceversa. In case is possible collect residual gases through a good separator and make a merging with residual gas collect in the right mode. The procedure for locating the best site to perform the sampling varies according to the type of manifestation in question.

Fumarole sampling
In this case, the most troublesome problems are represented by corrosion of the material, difficult access to the manifestation and the acid fumes that may envelop the field worker [2]. Determining the best site to perform such sampling is made on the basis of the flow rate and/or the maximum temperature found in the zone in question (from 100 to over 800 °C). Temperature measurements are performed with a thermocouple. If available, a titanium pipe should be introduced into the fissure; otherwise quartz tubes have been used successfully. It is unadvisable to use iron instruments for collecting the fluid because in the presence of a water condensate, the following reaction takes place:

\[
SO₂ + H₂O + Fe^{++} \rightarrow FeSO₃ + 2H^+
\]

The production of H₂, apart from increasing the concentration of this gas itself, also leads to serious errors in analyzing its isotopic composition. After having positioned the pipe, it should be sealed to avoid contamination by the surrounding air (the pipe is about 50 cm long). Then, after connecting the rubber tubing, it is advisable to wait for a few minutes, so that the fluid flowing through the tubes has a chance to heat them in order to avoid possible isotopic separation of the vapor. When sampling total gas (Fig. 3) the fluid must be made to flow through a condenser which holds
back the vapor. This is for two reasons: the first is that in a dry gas the reaction kinetics between H₂S and any O₂ is very low (with water acting as catalyst), while the second is that the condensed vapor and CO₂ are usually analyzed in the form of their stable isotopes, and the presence of humidity in the sample holder would be an index of a more or less pronounced degree of fractionation of the water collected. Moreover, fractionation of the O₂ in the CO₂ would be caused by isotopic exchange with the oxygen of the water present in the sample holder.

Proper sampling can generally be achieved by using two traps immersed in a solution of alcohol and dry ice that lowers the internal temperature to about −80 °C. An alternative refrigerant system that can be used, such as dipping the traps in either ice water or ether. The fluid passes through the traps before picking up the gas. Any vapor present condenses, thus being separated from the gas, which can then flow into the sample holder, on whose outlet a bubbler with a bit of Vaseline oil has been placed in order to check the regularity of flow.

Whenever the fluid does not issue forth with sufficient speed, the gas must be forced out with a peristaltic pump or a syringe connected to a "T" tap. Suction must be applied slowly, so as not to introduce air from the exterior.

Regarding residual gas, the sample holder is connected directly to the tube leading from the pipe (Fig. 4). The entry of vapor and the exothermal reaction between the NaOH solution and CO₂ causes an increase in temperature that slows the reaction. By cooling and gently shaking the sample holder, the process can be facilitated.

Using this method, all the fluid enters the bulb so that the gas/vapor ratio can be determined, as well as the constituent chemicals.
Useful suggestions for all types of sampling

In all sampling sessions, a log should be kept, not only of indications of a general nature, but of any problems encountered in order to aid in understanding eventual “anomalies” found in the analytical results. Moreover, it is also generally advantageous if the researcher conducting the analysis is also the same person who has prepared the sample holder and collected the fluids.

Transporting the sample holders

After each sampling, it must be checked that transportation of the samples to the laboratory does not accidentally cause the valve to break or open. The field worker who has performed the fluids collection should take care to apply some adhesive tape to keep the valves from twisting open (particularly the total gas samples because of their arrangement). Sample holders should be wrapped in paper or foam rubber and put in special shock-absorbing containers.

Analysis

Samples analysis is conducted primarily through gas chromatography techniques and, in the case of residual-gas CO₂, SO₂ and H₂S, the classical techniques of volume titration as well. Special sampling and analysis techniques are used for determining ammonia content.

General aspects of gas chromatography

Chromatography is a chemical-physical method of separation based on the equilibrium partition of the components to be separated, which are distributed between two phases: one fixed and the other mobile. The first is made up of a solid or opportunely supported liquid (stationary phase), while the second is represented by a fluid (mobile phase), containing the components to be separated, which percolate through the first. This method, discovered by the Russian botanist Tswett in 1906, who employed it to separate vegetables components, was introduced into the field of chemistry after some decades as an analytical method for separating various substances. Today it is applied in many areas of research and analysis and has been broadened to include numerous working techniques, all based on the same underlying principle, but differing in their practical application.

The term ‘chromatography’ comes from the fact that the first separations were performed using compounds that were distinguished on the basis of the various color changes they would undergo during the analysis.

Analytical techniques at the I.G.G.

In the laboratory of the I.G.G. two gas chromatographs are used: a Perkin Elmer model 3920 (1978) with thermoconductivity detector (TCD) and a P. E. model 8500 (1989) with flame ionization detector (FID) and catalyst. The detectors serve to transform the passage of each component of the gaseous mixture making up the eluate into an electric impulse. TCD detectors are non-specific and non-destructive, albeit not very sensitive; FID’s, instead, are very sensitive, but destructive (they burn combustible mixtures) and specific for hydrocarbons.
The analytical techniques currently used calls for employing various flow and temperature conditions and packed gas chromatographic columns suitable for the type of analyses being performed each time.

The two gas chromatographs are joined one to the other only by a “centralized variable volume” to which the gas in the sample holder is introduced (Fig. 5). Volume regulation allows using a range of volumes varying from 1 to 25 cc (from 26 to 50 cc considering the fixed volumes represented by the tubes and joints). Thus, it is possible to introduce a quantity of gas at fixed volume, but different pressures through the valves of the gas chromatographs (fig. 6), thereby varying the absolute amount. The system also includes a pressure gauge that provides pressure readings of the sample holder’s interior (in order to correct for expansion of the volume introduced).

The standardization technique used is external: gas mixtures of known concentration are prepared in the laboratory by taking the pure gases and mixing them in the suitable proportions. Mixing occurs in the two-valved sample holder fitted with a porous diaphragm. Such sample holders are filled to normal P with the same gas as that used as carrier, and the components of interest are added with a syringe through the porous diaphragm. The peaks obtained with the standards are used for comparisons with those of the samples in order to determine the percentage concentrations.

The laboratory tests we performed on the I.G.G.’s equipment revealed that the thermoconductivity detectors yield linear responses for all the components analyzed, from the limits of detectability up to a concentration of 100%. Such response, however, depends on not exceeding a gas insertion pressure of over 100 mBar, for which, except for particular cases, quantitative analyses are performed using very high concentrations, if not wholly pure specimens, of standard gas. Regarding the flame ionization detector, variable low concentrations of standards are instead used in order to determine the calibration curve for hydrocarbons and CO.
Table I: illustrates the instrument conditions

<table>
<thead>
<tr>
<th>COLUMN</th>
<th>T °C</th>
<th>DETECTOR</th>
<th>CARRIER</th>
<th>COMPONENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromosorb 2 m</td>
<td>50</td>
<td>TCD</td>
<td>He</td>
<td>CO₂, N₂O, H₂S</td>
</tr>
<tr>
<td>MS 5A 2 m</td>
<td>50</td>
<td>TCD</td>
<td>He</td>
<td>N₂, CH₄</td>
</tr>
<tr>
<td>MS 5A 2 m</td>
<td>-20</td>
<td>TCD</td>
<td>He</td>
<td>Ar, O₂</td>
</tr>
<tr>
<td>MS 5A 2 m</td>
<td>70</td>
<td>TCD</td>
<td>Ar</td>
<td>He, H₂</td>
</tr>
<tr>
<td>Silica Gel 2 m</td>
<td>50</td>
<td>FID+Catalyst</td>
<td>He</td>
<td>CO, CH₄</td>
</tr>
<tr>
<td>Chromosorb 2 m</td>
<td>60</td>
<td>FID</td>
<td>He</td>
<td>C₂ uns, C₂H₆, C₃H₆, C₃H₈</td>
</tr>
<tr>
<td>Chromosorb 2 m</td>
<td>100</td>
<td>FID</td>
<td>He</td>
<td>iso-C₄, iso-C₄ uns., n-C₄, n-C₄ uns</td>
</tr>
</tbody>
</table>

Legend:
- TCD: thermoconductivity
- FID + Catalyst: flame ionization with zirconium catalyst for reduction of CO
- FID: flame ionization

The Table 1 shows the component groups that can be analyzed under the various conditions. In the case of the I.G.G., two computers, three interfaces and two analysis programs by Perkin Elmer (Omega and Turbochrom) enable the analytical data to be collected, the concentrations calculated and any needed manual adjustments made.

Fig. 7: Separation of He (136 ppm) and H₂ (1378 ppm); the insertion pressure was 500 mbar.

Fig. 8: Separation of CO (6.1 ppm) and CH₄ (2.81%); the insertion pressure was 500 mbar.

Fig. 9: Separation of Ar (093%) and O₂ (20.95%) in the concentrations present in air. The working temperature of –20 °C requires raising the temperature to 50 °C between one analysis and the next in order to allow all components to be released and avoid phantom peaks in the subsequent run.

Fig. 10: Separation at 100 °C of 4-atom carbon compounds in the form of alkenes, as well as the isomers of their respective saturated compounds.
Fig. 7

Figure 8
The insertion line of the gas into the columns allows performing more than one analysis with the same sample portion, while at the same time enabling the pressure to be varied. Normally, the insertion pressure is 100 mbar. In order to analyze the components at low concentrations, the pressure can, if necessary, be increased even to over one atmosphere, thereby obtaining an increase in the absolute quantity of gas introduced into column.

**Wet analysis**

The liquid phase is extracted from the sample holder, its volume measured (V1) and it is maintained in a flask (usually 250 cc) which has been filled with Ar to avoid oxidation of the H₂S. A portion of this sample is used for CO₂ analysis [3].

**CO₂:**

The CO₂ content is determined in the form of HCO₃⁻ through titration with 0.1000 N HCl. The reaction is:

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2 \]

At pH 8.25, 99% of all the carbonate present is in the form of bicarbonate. At pH 3.8 all the bicarbonate is converted into CO₂. All other weak acids will add to the results of titration. Therefore, H₂S must be removed through sulfate oxidation using H₂O₂.

**Procedure:**

To a given volume, usually 20 cc, add 2-3 cc of H₂O₂ and bring the volume to 25 cc (V2). The sample is left to rest overnight and another portion (V3 - generally 5cc) of the oxidized sample transferred to a beaker. The pH is brought to a value of 8.25 using an HCl solution. The titration from pH 8.25 to pH 3.80 with a 0.1000 N solution of HCl yields the quantity of CO₂ present.

\[ \text{mM CO}_2 = \frac{V(\text{HCl}) \times N(\text{HCl}) \times V_2}{V_3} \times \frac{V_1}{V_2} \]

**H₂S**

H₂S is converted to Na₂S during the sampling and determined by means of the iodometric method. The sample is added to an acid solution of 0.1000 N I₂, whose volume is such that the resulting mixture remains acid even after the addition of the alkaline sample. It is then titrated with a solution of thiosulphate, according to the following reaction [4].
\[ S^\equiv + I_2 \rightarrow S^\circ + 2I^\equiv \]
\[ I_2 + 2H^\equiv + 2S_2O_3^\equiv \rightarrow S_4O_6^\equiv + 2HI \]

**Procedure:**

A sample volume \( V_5 \) is added to 10 cc of 5N H\textsubscript{2}SO\textsubscript{4}, together with a volume \( V_4 \) of an I\textsubscript{2} solution at known normality \( N(I_2) \). Titration is then performed with a thiosulphate solution of known \( N(t) \), until the starch water indicator changes color.

Calculating the meqs of H\textsubscript{2}S:

\[ \text{meq H}_2S = ((V_4*N(I_2) – V(t)*N(t))*V_1/V_4) \] (for mM divide the result obtained by 2).

**H\textsubscript{2}S and SO\textsubscript{2} in samples of volcanic origin**

The supernatant allows the iodometric determination of SO\textsubscript{2} according this reaction:

\[ I_2 + 2H^\equiv + 2S_2O_3^\equiv \rightarrow S_4O_6^\equiv + 2HI \]

Quantification of H\textsubscript{2}S is carried on by dissolving ZnS in H\textsubscript{2}O\textsubscript{2} and then using classic ponderal system of precipitation as BaSO\textsubscript{4} or ionic chromatographic system for determination of oxidized S\textsuperscript{\equiv} (SO\textsubscript{4}\textsuperscript{\equiv}).

**H\textsubscript{Cl} and HF in samples of volcanic origin**

Both components, H\textsubscript{Cl} and HF, normally presents in volcanic fluids are determined by liquid chromatography. Usually them are in large amount, so it is necessary to dilute the main idroxide solution, after oxidation with H\textsubscript{2}O\textsubscript{2}.

**Definitions of LOD and LOQ**

The limits of detectability and quantification \([5]\) in gas chromatography analyses are determined according to the guidelines set forth by the IUPAC (International Union of Pure and Applied Chemistry).

The limit of detectability (LOD), expressed in terms of concentration, is the smallest measurement that can be revealed with reasonable certainty with a given analytical procedure.

The limit of detectability is defined as \( n + 3s \), where \( n \) represents the average noise and \( s \) the standard deviation as determined through a suitably large number of measurements (20/30) of a meaningful baseline.

The limit of quantification (LOQ) of an analytical procedure is the smallest concentration of the target substance in a sample that can be determined quantitatively with an acceptable degree of precision and accuracy.
The limit of detectability is measured according to IUPAC standards and is expressed as $n + 10s$.

Application of these two parameters allows defining the threshold below which a compound is no longer detectable or quantifiable, respectively, with a reasonable degree of certainty.

**Calculation procedures**

The values of the limits described in the foregoing depend on the operating conditions (type and purity of the carrier gas, temperature and efficiency of the gas chromatograph column, etc.), the instrument's sensitivity, the quality of the detector, the noise inherent in the gas chromatographic column and the shape of the peaks. Moreover, given the same operating and instrument conditions, different retention times and thermal capacities (which vary for each analyzed gas) will result in substantially different limits.

The I.G.G. laboratory conducted an evaluation of the LOD and LOQ by inserting a standard gas into the valve loop at 1000 mBar, a method that it is not always possible or appropriate. By way of example, introducing the samples at 100 mBar would increase the values presented in Table 1 by a factor of 10 ($1000/100=10$).

The procedure adopted was that recommended by the IUPAC. As the LOD depends on both the peak height and the background noise, the average noise and the standard deviation were calculated in mV during a blank run for each group of components (Ar-O2, CO2-H2S, O2+Ar-N2-CH4, He-H2, C2-C3-C4) (figures 12, 13 and 14).

By introducing the standard components into the column at low concentrations, we were able to calculate the limits of detectability precisely by measuring the height of the various peaks (in mV).

The same procedure was adopted for calculation of the LOQ.

**Instrumentation of the I.G.G. laboratory**

Description of the gas chromatographic equipment in use at the I.G.G. laboratory

a) Gas chromatograph Perkin Elmer, model 3920 (year of purchase 1977) with thermistor detector (HWD). It is currently employed with a 2 meter-long, MS 5A column for the analysis of the components He-H2 under Ar (or N2) flow. It is also used for He flow analysis of the components CO2, H2S, Air, N2+O2, N2 , CH4, O2 and Ar. The columns utilized are a 2-meter Chromosorb 102 and a 2-meter MS 5A column.

b) Gas chromatograph Perkin Elmer, model 8550 (year of purchase 1988) with F.I.D. detector and zirconium catalyst. This is used for hydrocarbon and CO analysis. A 2 meter-long Silica gel column is utilized.

c) P.E. analysis and calculation programs (omega and turbochrom)
**Results obtained**

Tab. 2 – Performance measured according to IUPAC guidelines

<table>
<thead>
<tr>
<th>Component</th>
<th>LOD (ppm)</th>
<th>LOQ (ppm)</th>
<th>P intr. gas (mBar)</th>
<th>V loop (cc)</th>
<th>detector type</th>
<th>current (mA)</th>
<th>carrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>90</td>
<td>185</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>O₂</td>
<td>110</td>
<td>225</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>CO₂</td>
<td>40</td>
<td>85</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>H₂S</td>
<td>150</td>
<td>325</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>O₂+Ar</td>
<td>15</td>
<td>30</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>N₂</td>
<td>20</td>
<td>35</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>CH₄</td>
<td>45</td>
<td>80</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>225</td>
<td>He</td>
</tr>
<tr>
<td>CH₄ 0.1 0.15</td>
<td>1000</td>
<td>5</td>
<td>125</td>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.1</td>
<td>0.15</td>
<td>1000</td>
<td>5</td>
<td>FID</td>
<td>He</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>20</td>
<td>35</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>125</td>
<td>Ar</td>
</tr>
<tr>
<td>H₂</td>
<td>15</td>
<td>25</td>
<td>1000</td>
<td>1</td>
<td>HWD</td>
<td>125</td>
<td>Ar</td>
</tr>
<tr>
<td>C₂</td>
<td>0.05</td>
<td>0.08</td>
<td>1000</td>
<td>5</td>
<td>FID</td>
<td>He</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>0.04</td>
<td>0.07</td>
<td>1000</td>
<td>5</td>
<td>FID</td>
<td>He</td>
<td></td>
</tr>
<tr>
<td>C₄</td>
<td>0.03</td>
<td>0.06</td>
<td>1000</td>
<td>5</td>
<td>FID</td>
<td>He</td>
<td></td>
</tr>
</tbody>
</table>

Legend:  
- **FID** – Flame Ionization Detector  
- **HWD** – Hot Wire Detector  
- **P intr. gas** – Pressure at which the gas is introduced into the valve loop  
- **V loop** – Loop volume

Formula for determination of LOD₁ at insertion pressures (y) other than 1000 mBar: \( \text{LOD}_1 = \frac{\text{LOD} \times 1000}{(y)} \). Analogous formulas can be used for determining LOQ₁.

By way of example, figures 1, 2 and 3 furnish an idea of the noise inherent in the baseline measurements under different analytical and instrument conditions (the different scale magnifications in mV must be taken into account).

Fig. 11 shows the noise inherent in the 5A Molecular Sieve column under He flow (20 cc/min) at a temperature of –45 °C. It represents an example of calculation of the average noise in one sector of the baseline (to be performed 20/30 times).

Fig. 12 instead shows the noise inherent in the Chromosorb 102 column under He flow (20 cc/min) at a temperature of 50 °C. Such operating conditions are suitable for separating the components N₂+Ar+O₂ - CO₂ - H₂S.
Fig. 13 shows the noise inherent in the 2-meter, 5A Molecular Sieve column under Ar flow (30 cc/min) at a temperature of 60 °C. Such operating conditions are suited to separating the components He - H₂.
Defining the accuracy and precision of chemical analyses

Accuracy is a measure of the difference between the true value of a concentration and the experimentally determined one (fig. 14), and is usually expressed as relative percent error:

\[
100 \times \frac{\text{error}}{\text{true value}}
\]

The precision of a measurement (fig 14) is represented by the deviation of the values obtained from the mean, and is expressed as the standard deviation or relative percent deviation:

\[
100 \times \frac{\text{standard deviation}}{\text{mean of the values}}
\]

Determining the accuracy and precision of the gas chromatography analyses performed at the I.G.G. laboratory

In the specific case in question, we have calculated the analytical accuracy and precision of determinations of helium, hydrogen, oxygen, nitrogen and methane at varying concentrations. The concentration of each component was varied down to values approaching its LOQ and LOD and measured using a 5 A molecular sieve column in argon-flow, 2 m in length.

It should be noted that, although the working conditions were optimized for He and H₂ analyses, the other components can be analyzed by adopting different methodologies that guarantee high accuracy, precision and sensitivity.

The data presented in Table I have been obtained from a series of twelve consecutive analyses for each component. The practical usefulness resides in the fact that the
resulting values furnish the parameters serving to establish the general quality of the analysis and, above all, to define the range within which the analytical data may vary. It should be recalled that in He and H₂ analyses, the relative % error is about 2.5 for concentrations above the LOQ and rises to over 10% immediately below it.

Instrumentation and working conditions:

Gas chromatograph: Perkin Elmer mod. 3920
Detector: TCD at 100 °C and 125 MA
Carrier: Argon
Flow: 19 cc/min
Column: stainless steel, length 2 m, external diameter 1/8", filling MS 5 A 80/100 mesh.
Temperature: 70 °C, isothermal.

Table 3 – Accuracy and precision for H₂ and He

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Prepared Concentration (+/- 2%)</th>
<th>Accuracy Value found (total measures: 12)</th>
<th>Accuracy Relative error % (total measures: 12)</th>
<th>Precision S.D. (total measures: 12)</th>
<th>Precision % (+/-) (total measures: 12)</th>
<th>LOQ (ppm)</th>
<th>LOD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>100% 1536 ppm</td>
<td>100% 1479 ppm</td>
<td>0 %</td>
<td>0.35</td>
<td>0.35</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>768 =</td>
<td>750 =</td>
<td>3.7 %</td>
<td>12.8</td>
<td>0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>153.6 =</td>
<td>149.4 =</td>
<td>2.3 %</td>
<td>15.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.8 =</td>
<td>75 =</td>
<td>2.7 %</td>
<td>7.6</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.4 =</td>
<td>37.5 =</td>
<td>2.3 %</td>
<td>11.4</td>
<td>15.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% 1595 ppm</td>
<td>100% 153.9 ppm</td>
<td>0 %</td>
<td>0.27</td>
<td>0.27</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>153.8 =</td>
<td>153.9 =</td>
<td>3.7 %</td>
<td>10.1</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.5 =</td>
<td>39.4 =</td>
<td>0.1%</td>
<td>5.0</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.0 =</td>
<td>26.0 =</td>
<td>2.3 %</td>
<td>2.6</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.4 =</td>
<td>13.7 =</td>
<td>11.5%</td>
<td>2.1</td>
<td>9.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.0%</td>
<td>3.8</td>
<td>27</td>
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</tr>
<tr>
<td>O₂</td>
<td>2.095% 0.524% 0.209%</td>
<td>2.06% 0.487% 0.204%</td>
<td>1.1%</td>
<td>0.009</td>
<td>0.42</td>
<td>1000</td>
<td>300</td>
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<td></td>
<td>0.524%</td>
<td>0.487%</td>
<td>7.1%</td>
<td>0.014</td>
<td>2.81</td>
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<tr>
<td></td>
<td>0.209%</td>
<td>0.204%</td>
<td>2.4%</td>
<td>0.017</td>
<td>8.1</td>
<td></td>
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</tr>
<tr>
<td>N₂</td>
<td>7.81% 1.95% 0.781%</td>
<td>7.80% 1.99% 0.801%</td>
<td>0.1%</td>
<td>0.05</td>
<td>0.64</td>
<td>2000</td>
<td>1000</td>
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<tr>
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<td>1.95%</td>
<td>1.99%</td>
<td>2.1%</td>
<td>0.012</td>
<td>0.60</td>
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<tr>
<td></td>
<td>0.781%</td>
<td>0.801%</td>
<td>2.6%</td>
<td>0.023</td>
<td>2.80</td>
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</tr>
<tr>
<td>CH₄</td>
<td>9.63% 2.41% 0.963% 0.240%</td>
<td>9.64% 2.42% 0.988% 0.237%</td>
<td>0.1%</td>
<td>0.062</td>
<td>0.64</td>
<td>2500</td>
<td>1000</td>
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<tr>
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<td>2.41%</td>
<td>2.42%</td>
<td>0.4%</td>
<td>0.029</td>
<td>1.20</td>
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<tr>
<td></td>
<td>0.963%</td>
<td>0.988%</td>
<td>2.6%</td>
<td>0.032</td>
<td>3.24</td>
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<td>0.240%</td>
<td>0.237%</td>
<td>1.3%</td>
<td>0.014</td>
<td>5.91</td>
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</tbody>
</table>
References


4 - Lyberopoulou V., Mussi, Caprai 1992 – Training stage by Vera Lyberopoulou on geothermal and volcanic gas analyses, within the framework of the IAEA. Internal report I.G.G.

5 - IUPAC Compendium of chemical terminology (1997) 2nd edition